Intermediates Involved In O2 Activation By Iron-Porphyrin Catalysts: Role Of Hydrogen Bonding & Axial Ligation

Abstract

Nature uses different heme based enzymes for storage, transport and activation of oxygen. These enzymes have different functions based on difference in axial ligands and second sphere interactions like hydrogen bonding. In this thesis, a series of synthesized iron porphyrins with distal superstructures (enclosing a Hydrogen bonding cavity) have been used to understand the role of hydrogen bonding in catalysing oxygen reduction.

Resonance Raman has been used to find the Fe-O vibration of these complexes with hydrogen bonding distal pockets. The vibrations when compared with those reported, reveal that hydrogen bonding is responsible for strengthening Fe-O. Similarly, Fe-O vibrations of iron porphyrins with different axial ligands have been identified. These vibrations obtained from Resonance Raman experimentally demonstrate the “Push” effect. In yet another chapter, oxy adducts of cobalt corroles have been isolated and their Co-O vibrations compared with Fe-O vibrations of iron porphyrins.

One of the synthesized iron porphyrins (FeFc4) contain 4 electron donating ferrocene groups covalently attached to the porphyrin ring. This complex was found to catalyse reduction of O2 to O2− in an organic solvent and a selective 4e−/4H+ reduction of oxygen in aqueous. Further investigations show that the same catalyst can reduce O2 to H2O in the presence of a strong acid in organic medium and across all pH in aqueous. Thus, the same complex reduces O2 to H2O by 4 electrons but by different mechanisms in different solvents (PET in organic, PCET in aqueous).

The thesis also shows that Hydrogen bonding from 2nd sphere residues of an iron porphyrin to axial ligand like OH−, can strengthen or weaken the Fe-OH bond. The results explain how a weak FeIII-OH bond (due to Hydrogen Bonding) can lead to the stabilization of low spin ground state in synthetic mimics and in enzymes containing iron porphyrin active sites.

It is known that iron cannot bind oxygen in its stable +3 oxidation state. The mechanism of reduction of FeIII porphyrins to FeII form by hydrosulfide has also been investigated in this thesis.

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